COMPLETE SPECIFICATION.

Improvements in or relating to a Process for the Electrolytic Production of Fluorine and Apparatus therefor.

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for
5 which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to improvements in
10 or relating to a process for the electrolytic production of fluorine and apparatus therefor, and particularly to its production by electrolysis of a fused substantially dry mixture of potassium fluoride and hydrogen
15 fluoride having a composition approximating substantially to KF. 1.8 HF—KF. 2.2 HF.

It is well-known to manufacture fluorine by electrolysis of substantially dry fused mixtures of fluorides, in particular mixtures
20 of an alkali metal fluoride and hydrogen fluoride ("The present status of fluorine production", Chemistry and Industry 1956, pp. 504—511). Further in such processes it is well-known to use cells having anodes of
25 carbon or graphite, the cathode being of mild steel or other metal resistant to the action of the electrolyte. Hydrogen is evolved at the cathode and fluorine, with perhaps varying amounts of oxygen and other impurities, at
30 the anode. Also as mixtures of hydrogen and fluorine give rise to violent explosions such fluorine cells customarily have a diaphragm or partition designed to prevent mixing of the gases evolved at the two elec-
35 trodes. In some cells this diaphragm or partition extends downwards in the interelectrode space for a distance equal to or even greater than that of the downward ex-

tension of the electrodes. In other fluorine cells, for example, in that described and
40 claimed in United Kingdom Specification No. 668,465, a barrier, impervious to gases, extends downwards for a short distance only into the interelectrode space. However most of such cells of the types described above
45 have one feature in common, namely, an undesirably large distance between the anode and cathode.

It is, of course, well-known that the greater the spacing between the electrodes, the
50 greater must be the potential applied and the energy consumed to electrolyse a given amount of material and therefore it is desirable to diminish the interelectrode space as far as is commensurate with safety. Never-
55 theless it has hitherto been the consistent teaching in this art that (except in certain cells with unconventionally shaped electrodes, which are more fully described hereinafter) it is not possible safely to diminish
60 the distance between anode and cathode (hereinafter termed the electrode separation) or the distance between anode and gas barrier (hereinafter termed the anode gap) below certain limiting values. United
65 Kingdom Specification No. 668,465, for instance, which represents the most developed form of this teaching, propounds a rule that as the electrodes extend further downwards into the electrolyte below the
70 bottom of the gas barrier, the interelectrode spacing must be increased. It prescribes as absolute minima for safe working that when the electrodes extend to 8 inches below the gas barrier the electrode separation should
75 not be less than 2⅝ inches nor the anode gap less than 1 inch. The corresponding

values when the electrode are extended to 36 inches below the barrier are $4\frac{3}{4}$ inches and $1^{11}/_{16}$ inch. However, if a louvred cathode is used, the figures for the electrode separations appropriate to these depths of 8 inches and 36 inches may be diminished to $2\frac{1}{4}$ inches and $3^{15}/_{16}$ inches respectively. However, as said, these are prescribed as limiting minimum values and the spacings which it teaches should preferably be used for reliably safe working are appreciably greater than those prescribed minima.

In United Kingdom Specification No. 675,209 there is described and claimed a fluorine cell with an unusually small electrode separation, but in this cell an anode of unconventional design is employed. The upper portion of the anode, which lies wholly or partly below the electrolyte surface, is of smaller cross section than the main portion and extends above the level of the upper extremity of the cathode. A gas-impermeable bell or hood, conveniently of diameter equal to that of the main portion of the anode, dips into the electrolyte in the space between the cathode and this upper portion of the anode, entirely surrounding but not making contact with the latter. The fabrication of such anodes is however difficult or inconvenient and in practice these anodes are found to be embarrassingly fragile.

We have now found, most surprisingly, that it is possible safely, reliably and economically to work a fluorine cell with a substantially vertical solid carbon anode of substantially uniform cross-section and barrier of simple, robust, conventional design and employing current densities up to for example 1.1 amp./sq. in., using an anode gap much less than those which have hitherto been thought indispensible to safety if, said anode is permeable to gas and has a permeability of, for instance, between 1.0 and 30, permeability being here defined in terms of cubic feet of air per square foot of surface capable of passing through one inch thickness of the anode material per minute under an imposed pressure equivalent to two inches of water. The determination of the permeability is carried out on cylinders one inch diameter and one inch long. These cylinders are mounted tightly in a rubber holder and the mean of the measurements of the quantity of air passing through two cylinders, which are cut at right angles to one another from the same block, under an imposed pressure equivalent to 2 inches of water, is used to calculate the permeability. Ordinary electrode carbon measured in this way has a permeability of 0.05 and is unsuitable for the carrying out of the process of the present invention. Electrode carbon of such low permeability is considered to be impermeable for the purpose of the present invention.

According to the present invention the process for the production of fluorine by electrolysis at a temperature of 80°—110° C., preferably 80°—85° C., from a fused substantially dry mixture of potassium fluoride and hydrogen fluoride having a composition approximating substantially to KF. 1.8 HF—KF. 2.2 HF under non-polarization conditions and so that the composition of the mixture is maintained substantially at KF. 1.8 HF—KF. 2.2 HF, for example at a cathodic current efficiency of greater than 90% and preferably greater than 95%, with substantially no evolution of fluorine as free bubbles at a substantially vertical solid carbon anode of substantially uniform cross-section in conjunction with a gas impermeable barrier which dips below the surface of the electrolyte and which surrounds but is not in contact with the anode by employing current densities of e.g. 0.1 to 1.1 amperes per square inch and for instance effective lengths of anode and cathode up to e.g. 18 inches and in a cell in which the upper portion of the anode is above the level of the top portion of the cathode which is below the barrier, the top portion of the anode being partially or wholly below the surface of the electrolyte comprises providing for said carbon anode one which is gas permeable, and arranging that the horizontal distance between the anode and the cathode is from $\frac{3}{4}$ inch to 1.5 inch, that at least the lower extremity of the barrier is distanced, measured horizontally, by not more than $\frac{3}{8}$ inch from the anode, preferably that at least the lower extremity of the barrier approaches to within a distance, measured horizontally, of $^1/_{16}$ inch to $\frac{1}{8}$ inch from the anode, and that no portion approaches more nearly than $^1/_{16}$ inch.

Said cathode can be a plain sheet cathode or an apertured cathode e.g. a louvred cathode or one which consists of punched sheet or of gauze.

Preferably, for a plain sheet cathode its horizontal distance from the anode is arranged to be from $\frac{1}{2}$ inch to 1.5 inch.

To make sure said barrier is not in electrical contact with the anode it is sometimes desirable to provide insulating material in the space within the electrolyte between at least the lower extremity of the barrier and the anode.

The gas permeable carbon anode has to have at least a gas permeability such that substantially no free fluorine bubbles are liberated inter alia at the operating current density.

Preferably the permeability is approximately 30.

The term "effective anode length" refers to that portion of the anode length which is

below the gas barrier and is opposite to the effective length of the cathode.

Current density is determined with reference to that portion of the anode surface which is directly opposite the cathode.

The term "polarization" is used herein to denote the condition under which at a fixed voltage a sudden or gradual decrease occurs in the current flowing through the cell to a value which is a small fraction of that passing when the cell is operating normally. The effect may be temporary or permanent and is essentially an anodic phenomenon.

One form of an electrolytic cell adapted for the production of fluorine according to the process of the invention comprises a container for electrolyte, preferably provided with means serving for heating or cooling its contents, an electrolyte comprising a fued substantially dry mixture of potassium fluoride and hydrogen fluoride having a composition approximating substantially to KF. 1.8 HF to KF. 2.2 HF and a substantially vertical solid carbon anode of substantially uniform cross-section surrounded at its upper portion by, but not in contact with, a gas impermeable barrier dipping below the surface of the electrolyte and its lower portion by a wholly submerged plain sheet cathode which is below the said barrier and is characterised in that said carbon anode is gas permeable, and has, for instance, a gas permeability of between 1.0 and 30, in that the horizontal distance between the anode and the cathode (that is, the electrode-separation, as hereinbefore defined) is in the range $\frac{1}{2}$ inch to 1.5 inch, and in that at least the lower extremity of the barrier approaches to within a horizontal distance from the anode which is in the range $1/_{16}$ inch to $\frac{1}{8}$ inch and no portion approaches more nearly than $1/_{16}$ inch.

If in said form of electrolytic cell the plain sheet cathode is replaced by an apertured cathode e.g. a louvred cathode or one which consists of punched sheet or of gauze then the horizontal distance between the anode and the cathode is in the range of $\frac{3}{4}$ inch to 1.5 inch.

The dimension of the anode gap is related to the electrode separation which it is proposed to use. Thus a small electrode separation requires a small anode gap though any electrode separation above the minimum referred to herein may be used with the minimum anode gap quoted.

Preferably the barrier in the aforesaid form of cell has a downwardly and inwardly projecting slope or curve so shaped as to direct any hydrogen that rises from the cathode and comes into contact with the barrier upwardly and outwardly away from the anode.

The cathode should, preferably, as indicated in the aforesaid form of electrolytic cell, be wholly below the gas barrier. The vertical distance separating the upper extremity of the cathode from the lower extremity of the barrier is not critical but it must be adequate to allow of ready escape of hydrogen liberated in the space between anode and cathode. Clearly, if this vertical separation is inadequate, then when high current density is employed there is a possibility of a particularly brisk evolution of hydrogen leading to crowding of hydrogen bubbles within this space, so increasing the danger of hydrogen finding its way into the anode compartment. The requisite vertical separation of cathode and barrier is thus influenced not only by the spatial relationship of anode, cathode and barrier but also by the material of the anode and the current density at which the cell is to be operated. This vertical separation is not, however, a factor of major importance and a convenient practice is to make it of comparable magnitude with the electrode separation.

The anode, cathode and barrier may be cylindrical in form although other shapes, for instance of rectangular or square section, or even of hexagonal section, may be used if desired.

When working with such small clearances between the electrodes and the barrier as are specified above, robust and accurate construction, particularly of the gas barrier, is of considerable importance. One suitable type of barrier that may be employed when the anode is of cylindrical cross-section is a hollow cylinder made of a suitable metal with an inturned flange which is neither horizontal nor sloping upwards towards the anode, at the lower extremity extending inwards for such distance as to leave a clearance from the anode of the desired size. The anode barrier gap is in this case measured from the inner circumference of the flange to the face of the anode. Obviously the barrier may, if desired, be a simple hollow cylinder the flanged structure has, however, the advantage of greater rigidity which is obviously important when such small clearances are used. A flanged construction or one with a tapered or inturned lower extremity can be more reliably and precisely positioned with respect to the anode than a barrier which is only, say $1/_{16}$ inch, from the anode for its full length. Also not only is such an arrangement more resistant to deformation that would cause short-circuiting, but it virtually limits to very small dimensions the possible areas of contact that could be involved in short-circuiting between anode and barrier.

The body of the cell (i.e. the container), the gas barrier and the cathode may all conveniently be made from mild steel, although other materials resistant to the electrolyte

and the products of electrolysis may be used if desired. For instance, the barrier may be made of "Monel" (a Registered Trade Mark) or nickel.

The anode may be a simple block of carbon, whose minimum transverse dimension is at least $1\frac{1}{2}$ inches, preferably 2 inches. For, for instance, 60-amp. cells it may be convenient to use cylindrical anodes of diameter up to 3 inches; for 10-amp. cells, 2 inches is a convenient value. The length of the anode block is not of major importance. The point to be borne in mind in this connection is simply that if this total length be unduly great there will be an appreciable voltage drop as one proceeds down the anode from the lead-in conductor at the top towards the lower extremity, so that the effective potential difference between anode and cathode will not be as great in the lower portion of the cell as in the upper portion. The barrier is conveniently made 4 inches to 8 inches deep but can be greater or smaller if desired. It must dip sufficiently below the electrolyte surface to make an adequate liquid seal at the base of the anode (or fluorine) compartment — a depth of immersion of 2 inches is convenient. The length of the anode block that is "opposite to", and so in operative relationship with, the cathode, i.e. the effective lengths of the anode and cathode, is of more importance. We have used lengths ranging from 2 inches to $14\frac{1}{2}$ inches and find little difference in their effect apart from the voltage drop due to the ohmic resistance alluded to above. However, an unduly long and narrow interelectrode space can more easily lead to crowding of hydrogen bubbles if a high current density is used and also an increased length of carbon anode requires greater consideration to be given to its fragility.

The electrode separation, the depth of the interelectrode space, the current density employed, the material of which the gas permeable carbon anode is constructed and the size of the anode gap are all interconnected, but once the relevant principles are appreciated the appropriate adjustment of these various factors is a routine matter easily within the competence of the operator skilled in this art.

It is to be noted that the maximum current density which can be used will be dictated by the current density at which polarisation occurs and/or that at which breakaway of fluorine bubbles takes place.

Commercially available electrode carbons having a gas permeability of 25—30 and 10 respectively are eminently suitable.

High current density, a long narrow interelectrode space and an inadequate vertical clearance between the lower extremity of the barrier and the upper extremity of the cathode all tend to produce hydrogen crowd-

ing, but this can be avoided without increasing the electrode separation by increasing the vertical cathode-barrier clearance, shortening the electrodes and diminishing the anode gap. Thus, for instance, in operating one cell with a plain steel cathode and an anode of gas permeability 25—30, $14\frac{1}{2}$ inches long, using a current density of 1.0 amps./sq. inch and an electrode separation of $\frac{3}{4}$ inch, reliable working was obtained with an anode gap of $\frac{1}{8}$ inch. On diminishing the electrode separation to $\frac{1}{2}$ inch, the other conditions being unchanged, it was found necessary to reduce the anode gap to $^1/_{16}$ inch to achieve reliable working.

By adjusting these various factors appropriately as indicated, we have been able to construct cells having electrode separations and anode barrier gaps of the surpisingly small dimensions defined above which have given continuous trouble-free operation for periods as long as 9 months, and this without any need for electrode replacement or removal of sludge from the cell. The current efficiency was 97—98% using current densities up to 1.1 amp./sq. in.

The saving achieved on a standard 60-amp. cell consequent on reducing the electrode separation from the 2 inches hitherto employed to $\frac{1}{2}$ inch. with an 11 inch anode (i.e. below the bottom of the barrier) was 1.2 volts when operating at a current density of 0.6 amps./sq. inch and 1.9 volts when working at a current density of 0.9 amps./sq. inch.

The saving for an approx. 1400 amp. cell consequent on reducing the electrode separation from $2\frac{1}{2}$ inches to $1\frac{1}{4}$ inches with an 8 inch anode (i.e. below the bottom of the barrier) was 1.4 volts when operating at a current density of 0.5 amp./sq. inch and 2.5 volts when working at a current density of 0.9 amp/sq. inch.

The more detailed practice of the invention is illustrated by the following description.

One form of cell suitable for carrying out the invention is illustrated in the diagrammatic drawing accompanying the Provisional Specification which represents a vertical section through the said cell. Referring to the drawing, 1 is a container of mild steel or other suitably resistant metal, surrounded by a heating jacket 2 adapted for water, steam or electrical heating (water shown), and preferably thermostatically controlled. The lid 3 is insulated from the container 1 and from the carbon anode 4 by insulating material 5. The carbon anode 4 is partly submerged in the electrolyte 6. An electrically conducting rod 7 insulated from the cell lid 3 by insulating material 5 is connected to the anode 4. In close proximity to the anode 4 is a cathode 8 which may be of mild steel, copper or other material substantially resistant to the electrolyte 6 and products of electrolysis. The

cathode 8 may be a plain sheet, a louvred sheet, a punched sheet or gauze. When the cathode 8 is of punched sheet, it may be a sheet with $\frac{1}{4}$ inch diameter holes at $^3/_{16}$ inch centres. The cathode 8 is supported by an electrically conducting rod 9 passing through the top of the container 1. Attached to the lid 3 is a gas impermeable barrier 10 which surrounds that part of the anode 4 above the level of the top of the cathode 8. The pipe 11 for fluorine take-off is connected through the cell lid 3 to the space between the anode 4 and the gas barrier 10. The pipe 12 passing through the top of the container 1 is for take-off of hydrogen. The pipe 13 passing through the top of the container 1 into the electrolyte 6 is for addition of hydrofluoric acid.

The following examples of the working of such cells illustrate but do not limit the invention.

EXAMPLE 1.

The cell in this example comprises a jacketed mild steel vessel which is heated by hot water. The anode is cut from a block of carbon whose permeability is approximately 30, permeability being defined in terms of cubic feet of air per square foot of surface capable of passing through one inch thickness of the carbon per minute under an imposed pressure equivalent to two inches of water. The anode is of circular cross-section and of the following dimensions:—Diameter 3 inches, effective length $9^5/_8$ inches. An impermeable gas barrier of mild steel is situated only $^1/_{16}$ inch from the anode, while the cathode of mild steel is situated at a distance of only $^5/_8$ inch from the anode. The electrolyte is a mixture of hydrogen fluoride and potassium fluoride in the ratio HF:KF=1.8. The temperature of operation is 100° C.

The cell operates very smoothly at a current efficiency on fluorine of 90—95% for a period of 24 hours at an anode current density of 0.6 amp./sq. in. with an applied voltage of 7.3 volts. It may be mentioned by way of contrast that with an anode/cathode separation of three inches, as in a conventional cell, the applied voltage necessary to attain the same current density is 9.4 volts.

EXAMPLE 2.

The following table illustrates the voltage saving which is obtained with a 60-amp. cell having an anode gap of $1/_{16}$ inch as a result of reducing the electrode separation. The anode is $14\frac{1}{2}$ inches long and the electrolyte contains 40% HF. The cell is operated at 90° C. and the current efficiencies range from 98 and 100%.

Anodic Current Density (Amp./sq. in.)	Cell Voltage at Separation of			
	3″	1″	$\frac{3}{4}$″	$\frac{1}{2}$″
0.3	7.1	6.2	6.0	5.9
0.6	9.0	7.5	7.2	6.9
0.9	11.0	8.8	8.4	8.0

EXAMPLE 3.

The cell in this example comprises a rectangular mild steel vessel which is heated electrically by means of strip heaters on the outside of the vessel. The anode is cut from a block of carbon whose permeability is approximately 30. It is of rectangular cross-section, $2\frac{3}{4}$″ by 11″, and length $13\frac{1}{2}$″, the bottom 8″ length extending below an impermeable gas-barrier of nickel. The lower portion of the barrier is situated only $^1/_{16}$″ from the anode, while the mild steel cathode is situated at a distance of only $\frac{1}{2}$″ from the anode. The electrolyte is a mixture of hydrogen fluoride and potassium fluoride in the ratio HF:KF=2. The temperature of operation is 85° C.

The cell can be operated at loads up to 200 A (anodic current density of 0.95 A per square inch) for a total time of 1030 hours over a period of 6 months. Current efficiencies when determined during the period give results of 99—100% on fluorine. At 200 A the cell operates autothermally, with an applied voltage of 8.2 volt.

A second cell of identical size, but with the barrier placed $\frac{1}{4}$″ from the anode, and the cathode situated 2″ from the anode, operated autothermally at 170 A with an applied voltage of 9.9 volt. The operating voltage of the first cell at 170 A load is 8.0, showing a saving of 1.9 volt.

The fluorine from the cell with $\frac{1}{2}$″ electrode separation also contains less hydrogen fluoride than that from the cell with 2″ electrode separation. At 180 A load the results are 9.8 and 26.6% by volume, respectively.

EXAMPLE 4.

The cell in this example comprises a mild steel vessel containing twelve anodes of the same type and size of carbon as that in Example 3. The anodes are in pairs. Six impermeable gas barriers of nickel surround the upper portions of each of these pairs of anodes. The barriers are situated $\frac{3}{4}$″ from the anodes. Each pair of anodes has a pair of mild steel cathodes and each cathode is situated at a distance of $1\frac{1}{4}$″ from a pair of anodes. Provision is made for heating and cooling of the cell by circulating water through coils in the

cell. The electrolyte is a mixture of hydrogen fluoride and potassium fluoride in the ratio HF:KF=2. The temperature of operation is 85° C.

The cell can be operated continuously at a load of 2500 A (anodic current density of 1.1 A per square inch) for a period of at least 2 weeks. Current efficiency determinations during the period give results of 97—98% on hydrogen.

EXAMPLE 5.

The following table is a record of the results which have been obtained with an electrolytic cell according to the invention having a carbon anode of 1 inch diameter and of permeability 1.0 with an anode/cathode separation of one inch and an anode/barrier of $1/16$ inch.

Effective Anode Length (in)	Time of run (hour)	Anodic current density (A/in²)	Current Efficiency %
4	0.5	0.41	98.7
	0.9	0.41	99.7
2	0.4	0.77	99.0
	2.0	0.78	98.6
	1.7	0.79	98.5
	0.8	0.84	100.9
1	0.8	1.35	100.1
	1.1	1.87	99.9
	1.0	1.92	99.5

In one experiment an electrolytic cell according to the invention having two carbon anodes each of permeability 1.0 and of rectangular cross-section 2¾"×11" and length 13½", the bottom 8" extending below an impermeable gas-barrier of nickel, has operated for 45 days at a current density of 0.6 amp/sq. in. without the carbon anodes showing any sign of polarisation.

EXAMPLE 6.

The following table is a record of the results which have been obtained with an electrolytic cell according to the invention having a carbon anode of 1 inch diameter, of 2 inches effective length and of permeability 2.0 with an anode/cathode separation of one inch and an anode/barrier gap of $1/16$ inch.

Time of run (hour)	Anodic current (A/in²)	Current efficiency (%)
0.5	0.78	97.9
1.0	0.78	99.7
2.7	0.78	91.1
0.9	0.78	90.0
0.5	0.76	99.2
0.6	0.79	99.8
0.5	0.80	99.9

In one experiment an electrolytic cell according to the invention having two carbon anodes each of permeability 2.0 and of rectangular cross-section 2¾"×11" and length 13½", the bottom 8" extending below an impermeable gas-barrier of nickel has operated for 200 days at a current density of 0.7—1.1 amp/sq. in. without the carbon anodes showing any sign of polarisation.

In another experiment, in which the same carbon was used as anode, an electrolytic cell according to the invention, having an electrode separation of 1 inch and an anode/barrier gap of $1/16$ inch, had a current efficiency of 98 to 100% when operated at an anodic current density of up to 2.0 amp/sq. in.

WHAT WE CLAIM IS:—

1. A process for the production of fluorine by electrolysis at a temperature of 80—110° C. from a fused substantially dry mixture of potassium fluoride and hydrogen fluoride having a composition approximating substantially to KF. 1.8 HF−KF. 2.2 HF under non-polarisation conditions and so that the composition of the mixture is maintained substantially at KF. 1.8 HF−KF. 2.2 HF with substantially no evolution of fluorine as free bubbles at a substantially vertical solid carbon anode of substantially uniform cross-section in conjunction with a gas impermeable barrier which dips below the surface of the electrolyte and which surrounds but is not in contact with the anode and in a cell in which the upper portion of the anode is above the level of the top portion of the cathode which is below the barrier, the top portion of the anode being partially or wholly below the surface of the electrolyte which comprises providing for said carbon anode one which is gas permeable, and arranging that the horizontal distance between the anode and the cathode is from ¾ inch to 1.5 inch, that at least the lower extremity of the barrier is distanced, measured horizontally, by not more than ¾ inch from the anode, and that no portion approaches more nearly than $1/16$ inch.

2. A process as claimed in Claim 1

wherein the cathode is an apertured cathode. ,

3. A process as claimed in Claim 2 wherein the apertured cathode is a louvred cathode.

4. A process as claimed in Claim 2 wherein the apertured cathode consists of punched sheet or of gauze.

5. A process as claimed in Claim 1 wherein the cathode is a plain sheet cathode and the horizontal distance between the anode and the cathode is arranged to be from $\frac{1}{2}$ inch to 1.5 inch.

6. A process as claimed in any of the preceding claims wherein it is arranged that at least the lower extremity of said barrier approaches to within a distance, measured horizontally, of $^1/_{16}$ inch to $\frac{1}{4}$ inch from the anode.

7. A process as claimed in any of the preceding claims wherein insulating material is provided in the space within the electrolyte between at least the lower extremity of the barrier and the anode.

8. A process as claimed in any of the preceding claims wherein the cathodic current efficiency is greater than 90%.

9. A process as claimed in Claim 8 wherein the cathodic current efficiency is greater than 95%.

10. A process as claimed in any of the preceding claims wherein the temperature of the electrolyte is 80—85° C.

11. A process as claimed in any of the preceding claims wherein current densities are employed for the electrolysis lying between 0.1 and 1.1 amperes per square inch.

12. A process as claimed in any of the preceding claims wherein lengths of the anode and cathode below the level of the barrier are up to 18 inches.

13. A process as claimed in any of the preceding claims wherein the gas permeability is between 1.0 and 30.

14. A process for the production of fluorine by electrolysis substantially as described and with reference to the examples and the diagrammatic drawing accompanying the Provisional Specification.

15. An electrolytic cell for the production of fluorine comprising a container for electrolyte, an electrolyte comprising a fused substantially dry mixture of potassium fluoride and hydrogen fluoride having a composition approximating substantially to KF. 1.8 HF to KF. 2.2 HF and a substantially vertical solid carbon anode of substantially uniform cross-section surrounded at its upper portion by, but not in contact with, a gas impermeable barrier dipping below the surface of the electrolyte and at its lower portion by a wholly submerged plain sheet cathode which is below said barrier characterised in that said carbon anode is gas permeable, in that the horizontal dis-

tance between the anode and the cathode is in the range $\frac{1}{2}$ inch to 1.5 inch, and in that at least the lower extremity of the barrier approaches to within a horizontal distance from the anode which is in the range $^1/_{16}$ inch to $\frac{1}{4}$ inch and not portion approaches more nearly than $^1/_{16}$ inch.

16. An electrolytic cell for the production of fluorine comprising a container for electrolyte, an electrolyte comprising a fused substantially dry mixture of potassium fluoride and hydrogen fluoride having a composition approximating substantially to KF. 1.8 HF to KF. 2.2 HF and a substantially vertical solid carbon anode of substantially uniform cross-section surrounded at its upper portion by, but not in contact with, a gas impermeable barrier dipping below the surface of the electrolyte and at its lower portion by a wholly submerged apertured cathode which is below the said barrier characterised in that said carbon anode is gas permeable, in that the horizontal distance between the anode and the cathode is in the range $\frac{3}{8}$ inch to 1.5 inch, and in that at least the lower extremity of the barrier approaches to within a horizontal distance from the anode which is in the range $^1/_{16}$ inch to $\frac{1}{4}$ inch and no portion approaches more nearly than $^1/_{16}$ inch.

17. An electrolytic cell as claimed in Claim 16 wherein the apertured cathode is a louvred cathode.

18. An electrolytic cell as claimed in Claim 16 wherein the apertured cathode consists of punched sheet or of gauze.

19. An electrolytic cell as claimed in any of the Claims 15—18 wherein insulating material is provided in the space within the electrolyte between at least the lower extremity of the barrier and the anode.

20. An electrolytic cell as claimed in any of the Claims 15—19 wherein the gas permeability of the carbon anode is between 1.0 and 30.

21. An electrolytic cell as claimed in any of the Claims 15—20 wherein the barrier has a downwardly and inwardly projecting slope or curve so shaped as to direct any hydrogen that rises from the cathode and comes into contact with the barrier upwardly and outwardly away from the anode.

22. An electrolytic cell as claimed in any of the Claims 15—21 wherein means are provided for heating or cooling its contents.

23. An electrolytic cell substantially as described and with reference to the examples and the diagrammatic drawing accompanying the Provisional Specification.

ALFRED O. BALL,
Agent for the Applicants.

PROVISIONAL SPECIFICATION.

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hereinafter) it is not possible safely to diminish the distance between anode and cathode (hereinafter termed the electrode
60 separation) or the distance between anode and gas barrier (hereinafter termed the anode gap) below certain limiting values. United Kingdom Specification No. 668,465, for instance, which represents the most de-
65 veloped form of this teaching, propounds a rule that as the electrodes extend further downwards into the electrolyte below the bottom of the gas barrier, the interelectrode spacing must be increased. It prescribes
70 as absolute minima for safe working that when the electrodes extend to 8 inches below the gas barrier the electrode separation should not be less than $2\frac{5}{8}$ inches nor the anode gap less than 1 inch. The corre-
75 sponding values when the electrodes are extended to 36 inches below the barrier are $4\frac{3}{4}$ inches and $1 {}^{11}/_{16}$ inch. However, if a special louvred cathode is used, the figures for the electrode separations appro-
80 priate to these depths of 8 inches and 36 inches may be diminished to $2\frac{1}{4}$ inches and $3^{15}/_{16}$ inches respectively. However, as said, these are prescribed as limiting minimum values and the spacings which it teaches
85 should preferably be used for reliably save working are appreciably greater than these prescibed minima.

In United Kingdom Specification No. 675,209 there is described and claimed a
90 fluorine cell with an unusually small electrode separation, but in this case an anode of unconventional design is employed. The upper portion of the anode, which lies wholly or partly below the electrolyte sur-
95 face, is of smaller cross-section than the main portion and extends above the level of the upper extremity of the cathode. A gas-impermeable bell or hood, conveniently of diameter equal to that of the main por-
100 tion of the anode, dips into the electrolyte in the space between the cathode and this upper portion of the anode, entirely surrounding but not making contact with the latter. The fabrication of such special
105 anodes is however difficult or inconvenient and in practice these anodes are found to be embarrassingly fragile.

We have now found, most surprisingly, that it is possible safely, reliably and
110 economically to work a fluorine cell with a substantially vertical solid carbon anode of substantially uniform cross-section and barrier of simple, robust, conventional

design and employing current densities up to for example 1.1 amp./sq. in., using an anode gap much less than those which have hitherto been thought indispensible to safety if inter alia said anode has a permeability for instance of 10 and preferably of approximately 30, permeability being here defined in terms of cubic feet or air per square foot of surface capable of passing through one inch thickness of the anode material per minute under an imposed pressure equivalent to two inches of water. The determination of the permeability is carried out on cylinders one inch diameter and one inch long. These cylinders are mounted tightly in a rubber holder and the mean of the measurements on two cylinders which are cut at right angles to one another from the same block is taken as the permeability.

According to the present invention the process for the production of fluorine by electrolysis at a temperature of 80—110° C., preferably 80—85° C., from a fused substantially dry mixture of potassium fluoride and hydrogen fluoride having a composition approximating substantially to K.F 1.8 HF—KF. 2.2 HF under non-polarization conditions and so that the composition of the mixture is maintained substantially at KF. 1.8 HF—KF. 2.2 HF at a cathodic current efficiency of greater than 95%, with no evolution of fluorine as free bubbles at a substantially vertical solid gas permeable carbon anode of substantially uniform cross-section in conjunction with a gas impermeable barrier which entirely surrounds but is not in contact with the anode by employing current densities of e.g. 0.1 to 1.1 amperes per square inch for instance effective lengths of anode and cathode up to e.g. 15 inches and in a coil in which the horizontal distance of the cathode and the anode from the barrier is varied in accordance with the effective lengths of the anode and the cathode below the level of the barrier and the upper portion of the anode is above the level of the top portion of the cathode and is partially or wholly below the surface of the electrolyte is characterised in that the horizontal distance between the anode and the cathode is from ⅜ inch to 1.5 inch and in that at least the lower extremity of the barrier approaches to within a distance measured horizontally of $^1/_{16}$ inch to ⅜ inch from the anode and no portion approaches more nearly than $^1/_{16}$ inch.

The gas permeable carbon anode has to have at least a gas permeability such that no free fluorine bubbles are liberated inter alia at the operating current density.

Preferably the permeability is approximately 30.

The term "effective anode length" refers to that portion of the anode length which is below the gas barrier and is opposite to the effective length of the cathode.

Current density is determined with reference to that portion of the anode surface which is directly opposite the cathode.

The term "polarization" is used herein to denote the condition under which at a fixed voltage a sudden or gradual decrease occurs in the current flowing through the cell to a value which is a small fraction of that passing when the cell is operating normally. The effect may be temporary or permanent and is essentially an anodic phenomenon.

One form of an electrolytic cell adapted for the production of fluorine according to the process of the invention by electrolysis at a temperature of 80°—150° C., and preferably 80°—85° C., of a fused substantially dry mixture of potassium fluoride and hydrogen fluoride having a composition approximating substantially to KF. 1.8 HF to KF. 2.2 HF comprises a container for the electrolyte, preferably provided with means serving for heating or cooling its contents, electrolyte of the nature indicated and a substantially vertical solid gas permeable carbon anode of substantially uniform cross-section and of a gas permeability not less than 10 surrounded as to its upper portion by a gas impermeable barrier dipping below the surface of the electrolyte and as to its lower portion by a wholly submerged cathode which is below the said barrier and is characterised in that the horizontal distance between the anode and the cathode (that is, the electrode-separation, as hereinbefore defined) is in the range ½ to 1.5 inch when the cathode is a plain sheet cathode, and in the range ⅜ inch to 1.5 inch when the cathode is louvred or is made of punched sheet or gauze and in that at least the lower extremity of the barrier approaches to within a distance (measured horizontally) from the anode which is in the range $^1/_{16}$ inch to ⅜ inch and no portion approaches more nearly than $^1/_{16}$ inch.

The dimension of the anode gap is related to the electrode separation which it is proposed to use. Thus a small electrode separation requires a small anode gap though any electrode separation above the minimum referred to herein may be used with the minimum anode gap quoted.

In the aforesaid form of an electrolytic cell where the barrier has an inturned lower extremity and the distance of the main body of the barrier from the anode is greater than, equals or approaches the distance between the anode and the cathode, the lower extremity of the barrier is so shaped with a downwardly and inwardly projecting slope or curve as to direct any hydrogen that rises from the cathode and comes into contact with the barrier upwardly and outwardly away from the anode.

The cathode should, preferably, as indicated in the aforesaid form of electrolytic cell, be wholly below the gas barrier. The vertical distance separating the upper extremity of the cathode from the lower extremity of the barrier is not critical, but it must be adequate to allow of ready escape of hydrogen liberated in the space between anode and cathode. Clearly, if this vertical separation is inadequate, then when high current density is employed there is a possibility of a particularly brisk evolution of hydrogen leading to crowding of hydrogen bubbles within this space, so increasing the danger of hydrogen finding its way into the anode compartment. The requisite vertical separation of cathode and barrier is thus influenced not only by the spatial relationship of anode, cathode and barrier but also by the material of the anode and the current density at which the cell is to be operated. This vertical separation is not, however, a factor of major importance and a convenient practice is to make it of comparable magnitude with the electrode separation.

The anode, cathode and barrier may be cylindrical in form although other shapes, for instance of rectangular or square section, or even of hexagonal section, may be used if desired.

When working with such small clearances between the electrodes and the barrier as are specified above, robust and accurate construction, particularly of the gas barrier, is of considerable importance. One suitable type of barrier that may be employed when the anode is of cylindrical cross-section is a hollow cylinder made of a suitable metal with an inturned horizontal flange at the lower extremity extending inwards for such distance as to leave a clearance from the anode of the desired size. The anode gap is in this case measured from the inner circumference of the flange to the face of the anode. Obviously the barrier may, if desired, be a simple hollow cylinder; the flanged structure has, however, the advantage of greater rigidity which is obviously important when such small clearances are used. A flanged construction or one with a tapered or inturned lower extremity can be more reliably and precisely positioned with respect to the anode than a barrier which is only, say $^1/_{16}$ inch, from the anode for its full length. Also not only is such an arrangement more resistant to deformation that would cause short-circuiting but it virtually limits to very small dimensions the possible areas of contact that could be involved in short-circuiting between anode and barrier.

The body of the cell (i.e. the container), the gas barrier and the cathode may all conveniently be made from mild steel, although other materials resistant to the electrolyte and the products of electrolysis may be used if desired. For instance, the barrier may be made of "Monel" or nickel. Also when the larger values for the electrode separation are employed the cathode can conveniently be a simple hollow cylinder of mild steel. If, however, it is desired to work with an absolute minimum electrode separation, the cathode is preferably made either with louvred slots opening upwards and outwards away from the interelectrode space or it is made from punched sheet or gauze. Use of minimal values for the electrode separation also calls for minimal values for the anode gap and use of an appropriate material of construction for the anode, all as more fully discussed hereinafter.

The anode may be a simple block of carbon, whose minimum transverse dimension is at least $1\frac{1}{4}$ inches, preferably 2 inches. For, for instance, 60-amp. cells it may be convenient to use cylindrical anodes of diameter up to 3 inches; for 10-amp. cells, 2 inches is a convenient value. The length of the anode block is not of major importance. The point to be borne in mind in this connection is simply that if this total length be unduly great there will be an appreciable voltage drop as one proceeds down the anode from the lead-in conductor at the top towards the lower extremity, so that the effective potential difference between anode and cathode will not be as great in the lower portion of the cell as in the upper portion; clearly such conditions lead to a diminished energy efficiency (measured in terms of fluorine produced per unit of energy consumed) and hence are undesirable. The barrier is conveniently made 4 inches to 8 inches deep but can be greater or smaller if desired. It must dip sufficiently below the electrolyte surface to make an adequate liquid seal at the base of the anode (or fluorine) compartment—a depth of immersion of 2 inches is convenient. The length of the anode block that is "opposite to", and so in operative relationship with, the cathode, i.e. the effective lengths of the anode and cathode, is of more importance. We have used lengths ranging from 2 inches to $14\frac{1}{2}$ inches and find little difference in their effect apart from the voltage drop due to the ohmic resistance alluded to above. However, an unduly long and narrow interelectrode space can more easily lead to crowding of hydrogen bubbles if a high current density is used with an anode made of carbon of low permeability and also an increased length of carbon anode requires greater consideration to be given to its fragility.

The electrode separation, the depth of the interelectrode space, the current density employed, the material of which the gas permeable carbon anode is constructed and

the size of the anode gap are all interconnected, but once the relevant principles are appreciated the appropriate adjustments of these various factors is a routine matter easily within the competance of the operator skilled in this art.

Commercially available electrode carbons having a gas permeability of 25—30 and 10 respectively are eminently suitable.

High current density, a low narrow interelectrode space and an inadequate vertical clearance between the lower extremity of the barrier and the upper extremity of the cathode all tend to produce hydrogen crowding, but this can be avoided without increasing the electrode separation by increasing the vertical cathode-barrier clearance, shortening the electrodes and diminishing the anode gap. Thus, for instance, in operating one cell with a plain steel cathode and an anode of gas permeability 25—30, 14½ inches long, using a current density of 1.0 amps./sq. inch and an electrode separation of ¾ inch, reliable working was obtained with an anode gap of ⅛ inch. On diminishing the electrode separation to ½ inch, the other conditions being unchanged, it was found necessary to reduce the anode gap to $^1/_{16}$ inch to achieve reliable working.

By adjusting these various factors appropriately as indicated, we have been able to construct cells having electrode separations and anode gaps of the surprisingly small dimensions defined above which have given continuous trouble-free operation for periods as long as 9 months, and this without any need for electrode replacement or removal of sludge from the cell. The current efficiency was 97—98% using current densities up to 1.1 amp./sq. inch.

The saving achieved on a standard 60-amp. cell consequent on reducing the electrode separation from the 2 inches hitherto employed to ½ inch with an 11 inch anode (i.e. below the bottom of the barrier) was 1.2 volts when operating at a current density of 0.6 amps./sq. inch and 1.9 volts when working at a current density of 0.9 amps./sq. inch.

The saving for an approximate 1400 amp. cell consequent on reducing the electrode separation from 2½ to 1¼ inches with an 8 inch anode (i.e. below the bottom of the barrier) was 1.4 volts when operating at a current density of 0.5 amp./sq. inch and 2.5 volts when working at a current density of 0.9 amp./sq. inch.

The more detailed practice of the invention is illustrated by the following description.

One form of cell suitable for carrying out the invention is illustrated in the accompanying diagrammatic drawing which represents a vertical section through the said cell.

Referring to the drawing, 1 is a container of mild steel or other suitably resistant metal, surrounded by a heating jacket 2 adapted for water, steam or electrical heating (water shown), and preferably thermostatically controlled. The lid 3 is insulated from the container 1 and from the carbon anode 4 by insulating material 5. The carbon anode 4 is partly submerged in the electrolyte 6. An electrically conducting rod 7 insulated from the cell lid 3 by insulating material 5 is connected to the anode 4. In close proximity to the anode 4 is a cathode 8 which may be of mild steel, copper or other material substantially resistant to the electrolyte 6 and products of electrolysis. The cathode 8 may be a plain sheet, a louvred sheet, a punched sheet or gauze. When the cathode 8 is of punched sheet, it may be a sheet with ⅛ inch diameter holes at $^3/_{16}$ inch centres. The cathode 8 is supported by an electrically conducting rod 9 passing through the top of the container 1. Attached to the lid 3 is a gas impermeable barrier 10 which surrounds that part of the anode 4 above the level of the top of the cathode 8. The pipe 11 for fluorine take-off is connected through the cell lid 3 to the space between the anode 4 and the gas barrier 10. The pipe 12 passing through the top of the container 1 is for take-off of hydrogen. The pipe 13 passing through the top of the container 1 into the electrolyte 6 is for addition of hydrofluoric acid.

The following examples of the working of such cells illustrate but do not limit the invention.

EXAMPLE 1.

The cell in this example comprises a jacketed mild steel vessel which is heated by hot water. The anode is cut from a block of carbon whose permeability is approximately 30, permeability being defined in terms of cubic feet of air per square foot of surface capable of passing through one inch thickness of the carbon per minute under an imposed pressure equivalent to two inches of water. The anode is of circular cross-section and of the following dimensions:— Diameter 3 inches, effective length 9⅝ inches. An impermeable gas barrier of mild steel is situated only $^1/_{16}$ inch from the anode, while the cathode of mild steel is situated at a distance of only ⅛ inch from the anode. The electrolyte is a mixture of hydrogen fluoride and potassium fluoride in the ratio HF:KF=1.8. The temperature of operation is 100° C.

The cell operates very smoothly at a current efficiency on fluorine of 90—95% for a period of 24 hours at an anode current density of 0.6 amp/sq. inch with an applied voltage of 7.3 volts. It may be mentioned by way of contrast that with an anode/cathode separation of three inches, as in a

conventional cell, the applied voltage necessary to attain the same current density is 9.4 volts.

EXAMPLE 2.

The following table illustrates the voltage saving which is obtained with a 60-amp. cell having an anode gap of $^1/_{16}$ inch as a result of reducing the electrode separation. The anode is $14\frac{1}{2}$ inches long and the electrolyte contains 40% HF. The cell is operated at 90° C. and the current efficiencies range from 98 and 100%.

Anodic Current Density (Amp./sq. in.)	Cell Voltage at Separation of			
	3″	1″	$\frac{3}{4}$″	$\frac{1}{2}$″
0.3	7.1	6.2	6.0	5.9
0.6	9.0	7.5	7.2	6.9
0.9	11.0	8.8	8.4	8.0

EXAMPLE 3.

The cell in this example comprises a rectangular mild steel vessel which is heated electrically by means of strip heaters on the outside of the vessel. The anode is cut from a block of carbon whose permeability is approximately 30. It is of rectangular cross-section, $2\frac{3}{4}$″ by 11″, and length $13\frac{1}{2}$″, the bottom 8″ length extending below an impermeable gas-barrier of nickel. The lower portion of the barrier is situated only $^1/_{16}$″ from the anode, while the mild steel cathode is situated at a distance of only $\frac{1}{2}$″ from the anode. The electrolyte is a mixture of hydrogen fluoride and potassium fluoride in the ratio HF:KF=2. The temperature of operation is 85° C.

The cell can be operated at leads up to 200 A (anodic current density of 0.95 A per square inch) for a total time of 1030 hours over a period of 6 months. Current efficiencies when determined during the period give results of 99—100% on fluorine. At 200 A the cell operates automatically, with an applied voltage of 8.2 volt.

A second cell of identical size, but with the barrier placed $\frac{1}{4}$ inch from the anode, and the cathode situated 2″ from the anode, operates autothermally at 170 A with an applied voltage of 9.9 volt The operating voltage of the first cell at 170 A load is 8.0, showing a saving of 1.9 volt

The fluorine from the cell with $\frac{1}{2}$″ electrode separation also contains less hydrogent fluoride than that from the cell with 2″ electrode separation. At 180 A load the results are 9.8 and 26.6% by volume, respectively.

EXAMPLE 4.

The cell in this example comprises a mild steel vessel containing twelve anodes of the same type and size of carbon as that in Example 3. The anodes are in pairs. Six impermeable gas barriers of nickel surround the upper portions of each of these pairs of anodes. The barriers are situated $\frac{3}{4}$″ from the anodes. Each pair of anodes has a pair of mild steel cathodes and each cathode is situated at a distance of $1\frac{1}{4}$″ from a pair of anodes. Provision is made for heating and cooling of the cell by circulating water through coils in the cell. The electrolyte is a mixture of hydrogen flouride and potassium fluoride in the ratio HF:KF=2. The temperature of operation is 85° C.

The cell can be operated continuously at a load of 2500 A (anodic current density of 1.1 A per square inch) for a period of at least 2 weeks Current efficiency determinations during the period give results of 97—98% hydrogen.

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Agent for the Applicants.

852,369   PROVISIONAL SPECIFICATION
I SHEET   *This drawing is a reproduction of
the Original on a reduced scale.*